Development of Soybean Oil-Based Composites by Solid Freeform Fabrication Method: Epoxidized Soybean Oil with Bis Or Polyalkyleneamine Curing Agents System

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ABSTRACT: Soybean oil-based composites are prepared by the solid freeforming fabrication (SFF) method. Epoxidized soybean oil is solidified with a gelling agent, and composites are formed by fiber reinforcement. Glass, carbon, and mineral fibers are used in the formulations. The type of fiber and degree of fiber alignments affect the properties of the composites. In addition, the effects of curing agents, curing temperature, fiber combination, and fiber loading on mechanical properties of composites and dynamic analysis are studied and reported. © 2002 Wiley Periodicals, Inc.* J Appl Polym Sci 85: 2100–2107, 2002

Key words: epoxidized soybean oil; solid freeforming fabrication; fiber reinforcement; curing agents; fiber combination

INTRODUCTION

Concerns for the stability of future petroleum supplies has stimulated much attention in the past a few decades to feedstocks for polymers based on renewable resources.[1–3] More recently, the importance of natural products for industrial applications becomes very clear with increasing emphasis on the environmental issues, waste disposal, and depleting nonrenewable resources. United States agriculture produces >16 billion pounds of soybean oil annually, only 500 million pounds of which is used in industrial application, and frequently carry-over exceeds 1 billion pounds. Development of economically feasible new industrial products from soybean oil or commercial processes is highly desirable. Soy-based polymers could support global sustainability and provide an alternative to synthetic polymers for many manufacturing applications.[4]

Solid freeforming fabrication (SFF) is a method of making shapes without molds. It is best known in its stereolithography forms as a method of rapid prototyping. In stereolithography, a laser photopolymerizes successive thin layers of monomer to build up a solid object. The reactive extrusion freeforming technique was developed by Calvert and co-workers.[5] In this system, a liquid or particle slurry is dispensed by syringe into a two-dimensional (2-D) pattern. A motorized table is mounted on an x–y drive. In the format used in this project, a stepper-motor driven syringe is mounted above the table, with both controlled

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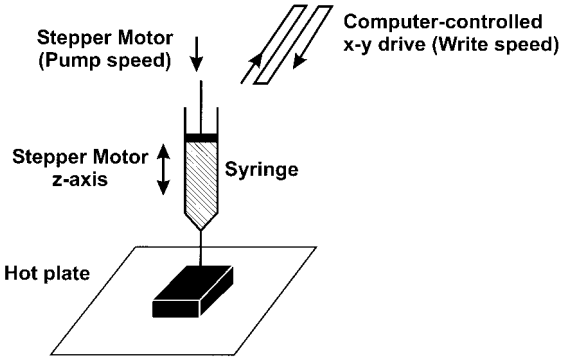

Figure 1 Sketch of the extrusion freeform fabrication apparatus.

from a computer. The process is analogous to the use of a pen plotter for writing a 2-D pattern (Figure 1). The shape to be produced may be derived from a 3D CAD program or from standard drawing packages.

Soybean oil is mainly a mixture of triacylglycerides that are esters of glycerol with various saturated and unsaturated fatty acids. The double bonds in unsaturated fatty acids may be converted into the more reactive oxirane moiety by reaction with peracids or peroxides. In the past, epoxidized soybean oil (ESO) has mainly been used as a plasticizer for polyvinyl chloride (PVC) compounds, chlorinated rubber, and polyvinyl alcohol (PVA) emulsions. Epoxy-containing soybean oil used as raw materials for the synthesis of new polymers suitable for liquid molding processes have been reported by Wool and co-workers.[6,7] The preparation of structurally strong ESO-based composites is attractive from both the commercial and environmental perspectives. In addition, mineral fillers and fibers are now extensively used in the plastics industry to achieve desired properties or to reduce the price of the finished articles. In contrast to typical petroleum-based composite matrix resins, such as vinyl esters, polyesters, and epoxies, soy-based composites are optionally biodegradable; as plant oils, they contain functional groups that are readily attacked by lipase-secreting bacteria. We have prepared soy-based polymers ranging from soft rubbers to hard plastics.[8] In this paper, the development of epoxidized soybean oil-based composites with soft rubber properties by embedding strong fibers (e.g., glass and carbon) and mineral fibers (calcium sulfate microfiber and Wollastonite mineral fiber) are reported using the SFF method.

EXPERIMENTAL

Materials

ESO was obtained from Elf Atochem Inc. (Philadelphia, PA) and used as received. Calcium sulfate microfiber, Franklin Fiber® H-45, used in the experiments was provided by the United States Gypsum Company, (Chicago, IL). Wollastonite mineral fiber, Fillex® 17-AF1 fiber, is a surface-modified Wollastonite, an inorganic mineral reinforcement, and was provided by Intercorp Inc., (Milwaukee, WI). Thixotropic agent, Aerosil R805, was purchased from Degussa Corp. (Ridgefield Park, NJ). Milled E-glass (electric glass) fiber with a nominal length of 1/32 in. and fiber diameter of 10 μm was used. Curing agents, 2,2'-(ethylenedioxy)-bisethylamine, Jeffamine EDR-148, polyalkyleneamine, Jeffamine D-230, and Jeffamine T-403 were provided by Huntsman Corp. (Houston, TX). Diethylenetriamine (DETA) and triethylenetetramine (TETA) were provided by Aldrich Chemical Inc. (Milwaukee, WI). All the chemicals and fibers were used without further purification. Short carbon fiber was obtained from Dupont Company (Wilmington, DE) and was chopped in a coffee grinder for 40 s to reduce the length. Optical microscopy gave an average length of $\sim$0.16–0.10 mm. A previous study[9] characterized length distributions, diameter distributions, and aspect ratios obtained for fibers chopped in this way.

Composite Formation

ESO was mixed with Aerosil R805 thixotropic agent (13 g/100 g ESO), and fibrous fillers. The mixture was degassed in a vacuum system at 55 °C for 30 min. The fiber filled slurries show a yield point such that formed parts hold their shape until cured. The mixture was removed from the oven and cooled to room temperature. Curing agent (37 g/100 g ESO) was added and mixed properly; the paste was then put into a 20-cc plastic syringe. Bars (75 $\times$ 8 $\times$ 4 mm) were formed by deposition of five layers and were subsequently cured at 100 °C for 24 h and then at 150 °C for 48 h.

Solid Freeform Fabrication

Solid freeform fabrication was conducted using an Asymtek model 402 fluid dispensing system equipped with small stepper motors (Oriel stepper mike) to drive the delivery syringe. The

Asymtek and syringe were controlled by a program written in Microsoft Quick Basic. Solid bar samples were written as a series of lines.

Tensile Tests

The nonlinear mechanical behavior of the fiberous/soybean oil-based composites was analyzed with an Instron model IX automated materials testing system in tensile mode, with a load cell of 1000 N capacity. The crosshead speed was 50 mm/min. The specimen was a thin rectangular strip (75 × 8 × 4 mm). Tensile tests were performed at 25 °C. Young's modulus (E) was measured from the low strain region. The values reported in this study are the average of five measurements.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) was performed with a JEOLJSM 6400V instrument to investigate the morphology of the different kinds of fibers and the interface between the filler and the polymeric matrix. The specimens were mounted on aluminum stubs with graphite-filled tape and vacuum-coated with gold-palladium on a JEOL ion sputter coater, and observed. SEM micrographs were obtained using 5 kV secondary electrons.

Dynamic Mechanical Analysis

Dynamic mechanical tests were carried out with a Perkin Elmer DMA 7 spectrometer in the three-point bending mode. The tests were performed at 1.0 Hz of frequency, and the temperature was varied between −60 and 60 °C in 5 °C increments. The specimen was a thin rectangular strip with dimensions of 15 × 3.5 × 2 mm.

RESULTS AND DISCUSSION

Morphological Characterization

SEM was performed to characterize both the structure and the morphology of the four kinds of fibers used in the soybean oil-based filled composite materials.

Fiber Structure

SEM micrographs in Figure 2 show the structure of the pure fibers. Figure 2(a) corresponds to commercial milled glass fibers with a nominal length of 1/32 in. and fiber diameter of 10 μm. The aspect ratio distribution of milled glass fiber determined by Peng[10] shows two main peaks at 3 and 7. Figure 2(b) corresponds to calcium sulfate microfiber, Franklin Fiber® H-45. Franklin Fiber® H-45 microfiber is a single crystal fiber made from high purity gypsum, calcium sulfate dihydrate, by a patented hydrothermal synthesis into an acicular crystal. After analyzing Franklin Fiber® H-45 sample, their physical properties were determined as follows: average length of 60–75 μm, average diameter of 1.5–2 μm, average aspect ratio of 40. Figure 2(c) corresponds to Wollastonite mineral fiber, Fillex® 17-AF1 fiber. The Fillex® 17-AF1 fiber is surface-modified Wollastonite mineral fiber. After analyzing Fillex® 17-AF1 fiber sample, their physical properties were identified as average aspect ratio of 20, and diameter of 2.5 μm. Figure 2 (d) corresponds to carbon fiber. The carbon fiber was ground for 40 s in a coffee grinder. Optical microscopy gave average lengths from 0.16 to 0.10 mm.

Composite Morphology

SEMs of freshly fractured surface for a soybean oil-based composite filled with four kinds of fibers are shown in Figure 3. Fiber concentration of the composite is 12 vol %. Figure 3(a) corresponds to composite filled with milled glass fiber. Figure 3(b) corresponds to composite filled with Franklin fiber® H-45. Figure 3(c) corresponds to composite filled with Fillex® 17-AF1 fiber. Figure 3(d) corresponds to composite filled with carbon fiber. These results clearly indicate a good interfacial adhesion between the fiber and matrix that can be readily seen from the physical contact between both components. The fibers are broken up from the matrix. However, holes and spacing occur along the fiber, resulting in poor contact and inferior stress transfer between the phases.

Effect of Curing Temperature

Effect of curing temperature on the mechanical properties of composite filled with Franklin fiber® H-45 is presented in Table I. As can be seen, that Young's modulus increases as the curing temperature increases because at lower temperature, the epoxy groups are mainly consumed by primary amine, but secondary amine reaction was relatively small. Padma and co-workers[11] reported an intensity increase in the secondary amine peaks by Fourier transform infrared (FTIR), compared

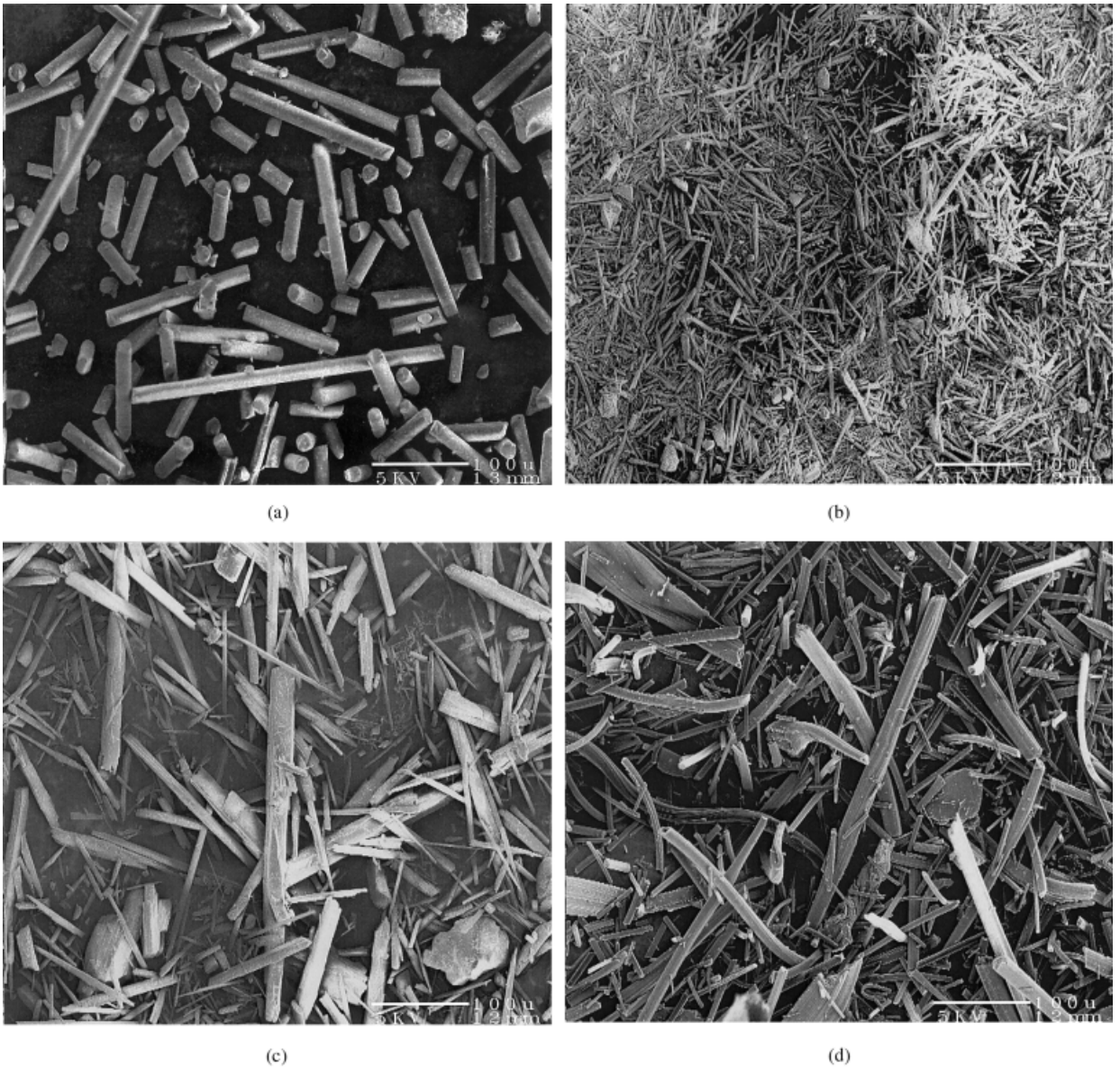

Figure 2 Scanning electron microscope (SEM) photomicrograph of the four kinds of fibers used in present in the study: (a) E-glass fiber, (b) Franklin fiber® H-45, (c) Wollastonite, Fillex® fiber, (d) carbon fiber.

with primary amine peaks. At higher temperature, both primary and secondary amine reacted with epoxy groups. As the reaction proceeds further, the epoxy-hydroxyl etherification reaction dominated the reaction. With increased crosslinking degree, the composites get better mechanical properties.

Effect of Different Types of Fibers

Four different kinds of fibers were used in the composite formulations. With fiber concentration at 12 vol %, the mechanical properties of the composite were determined, as shown in Table II. It can be seen that among different fiber types, glass fiber and carbon fiber show better reinforcing effects than the mineral fibers, Franklin Fiber® H-45, and Wollastonite fiber, Fillex® 17-AF1. It is well known that composites properties are greatly dependent on modulus of fiber as well as on fiber length and aspect ratio. Because E glass fiber has a tensile strength of 3 GPa and a modulus that approaches 100 GPa, it exhibits a large

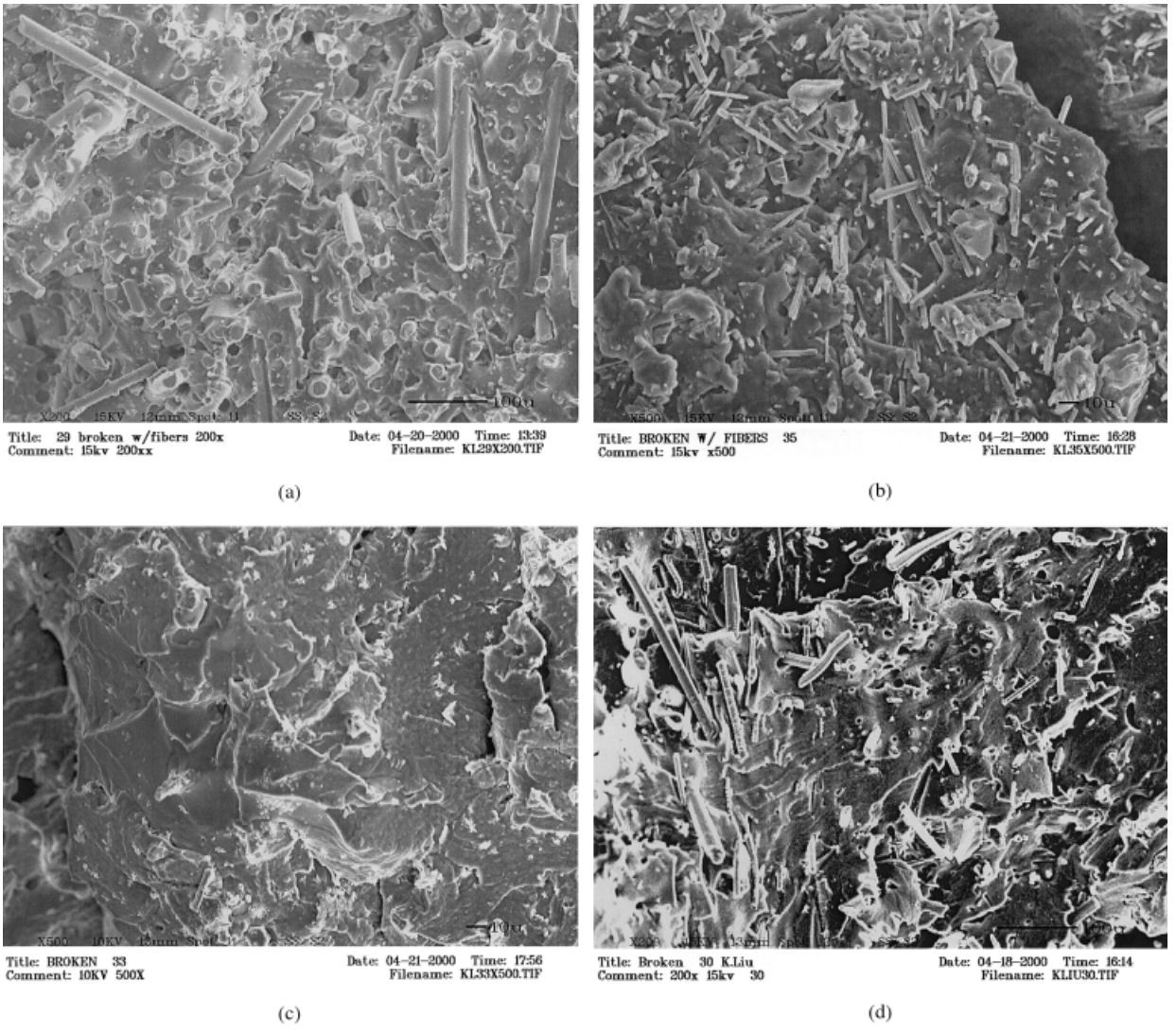

Figure 3 Scanning electron micrograph of the freshly fractured surface of soybean oil-based composites filled with four kinds of fiber: (a) composite filled with E-glass fiber, (b) composite filled with Franklin fiber® H-45, (c) composite filled with Wollastonite, Fillex® fiber, and (d) composite filled with carbon fiber.

contribution to the strength and rigidity of the reinforced composites.

Effect of Curing Agent

The Young's modulus data for a composite consisting of ESO (52 wt %), Franklin fiber (22 wt %), and curing agent (37 g/100 g ESO) are shown in Table III. When Jeffamine D-230 is used as curing agent, the composite has lower physical properties. This result was presumably due to the reactivity of the amine groups in the Jeffamine D-230 (polyoxypropylenediamine), where the amine groups are located on secondary carbon atoms at the ends of an aliphatic polyether chain. In contrast, the amine groups of Jeffamine EDR-148 (triethyleneglycoldiamine) are located on primary carbon atoms at the ends of an aliphatic polyether chain. The product is an unhindered diamine that is miscible in a wide variety of solvents and much more reactive than Jeffamine D-230. Jeffamine T-403 (polyoxypropylenetriamine) is a trifunctional primary amine. Its amine groups are located on secondary carbon atoms at the ends of aliphatic polyether chains. The reactivity of amines located on secondary carbon atoms is weaker than that of amines located

Table I Effect of Curing Temperature[a]

Temperature (°C)	Tensile Strength (MPa)	Tensile Modulus (MPa)
130	0.72	2.18
140	1.02	4.30
150	1.52	7.20
160	1.40	8.81

[a] Conditions: ESO, 56 wt %; Franklin fiber, 15.6 wt %; Jeffamine EDR-148, 37 g/100 g ESO; fumed silica, 13 g/100 g ESO.

Table III Effect of Curing Agent[a]

Curing Agent	Tensile Strength (MPa)	Tensile Modulus (MPa)	Epoxy/ Amine H
Jeffamine D230	0.11	1.01	1:1.47
Jeffamine T403	1.25	7.5	1:1.26
Jeffamine EDR 148	1.43	8.00	1:2.28
DETA	6.29	231.39	1:4.10
TETA	8.29	301.60	1:2.10

[a] Conditions: ESO 52 wt %; Franklin fiber, 22 wt %; curing agent, 37 g/100 g ESO; fumed silica, 13 g/100 g ESO.

on primary carbon atoms. As can be seen from physical properties in Table III, the reactive order is EDR-148 > T-403 > D230. Compared with the Jeffamine curing agent, TETA and DETA have better physical properties (see Table III). The reason for this difference is that there are two primary amine groups located on primary carbon atoms at the ends of an aliphatic polyimine chain in TETA and DETA. At same time, there is one secondary amine group in DETA and two secondary amine groups in TETA. Those secondary amine groups also take part in crosslinking reaction and formulate a network structure of polymer matrix. A network structure of polymer matrix provides strong mechanical properties of composites. Soy-based composites with tough and rigid plastics properties, created with TETA and DETA as curing agents, will be reported in our next publication.[8]

Influence of Fiber Orientation on Young's Modulus

The strength and moduli of fiber-reinforced composites depend on fiber volume fraction, aspect ratio, and orientation. Direction of reinforcement is critical in determining the mechanical properties of a composite. Strength as well as stiffness follows the direction of the reinforcement. To explore the effect of orientation on the properties of composites, test bars were made by writing at varying angles relative to the axis of the test bars. The effect of this orientation on elastic modulus is shown in Table IV. It can be seen that modulus is doubled when the fiber axis is parallel to the writing direction compared with the modulus with an axis across this writing direction. The large difference between longitudinal and transverse moduli is familiar in many types of composites.

Effect of Fiber Combination

The research development in the use of mineral fibers has been limited to a single type and their usage in thermoplastic matrix or elastomers. The combination of glass or carbon fiber with mineral fiber in a thermoset matrix has recently been investigated by Peng.[10] Experimental results suggest that combining different fiber types into testing bars tends to get higher flexural modulus

Table II Tensile Test Results of Composites with Different Types of Fibers[a]

Fiber	Tensile Strength (MPa)	Tensile Modulus (MPa)
E-glass fiber	1.50	12.2
Carbon fiber	1.45	9.3
Franklin Fiber® H-45	1.43	9.1
Fillex® 17-AF1	1.30	9.0

[a] Conditions: fiber, 12 vol %; Jeffamine EDR-148, 37 g/100 g ESO; fumed silica, 13 g/100 g ESO.

Table IV Influence of Fiber Orientation on Tensile Modulus[a]

Angle of Writing Direction of Axis to Tension, degrees	Tensile Strength (MPa)	Tensile Modulus (MPa)
0	1.51	7.20
30	1.49	7.05
45	1.27	4.71
60	0.89	4.26
90	0.88	4.18

[a] Conditions: ESO 56 wt %; Franklin fiber, 15.6 wt %; curing agent, 37 g/100 g ESO; fumed silica, 13 g/100 g ESO.

Table V Effect of Fiber Combination[a]

Fiber Combination	Tensile Strength (MPa)	Tensile Modulus (MPa)
Glass fiber (44 wt %) and Franklin fiber H-45 (7 wt %)	18.21	794.81
Carbon fiber (20 wt %) and Franklin fiber H-45 (8.5 wt %)	11.30	528.68

[a] Conditions: curing agent, 37 g/100 g ESO; fumed silica, 13 g/100 g ESO.

compared with single-type fiber–epoxy composites. Here, we studied the fiber combination such as short milled glass fibers (1/32 in.) and Franklin Fiber® H-45, as well as short carbon fibers and Franklin Fiber® H-45. The results of these experiments, shown in Table V, clearly demonstrate that moduli of the composites increase by combining two types of fiber rather than using one type of fiber. These experimental results confirm the theory that combining different fiber types in testing parts gives higher flexural modulus compared with single-type fiber–ESO composites. By utilizing the packing concepts, the use of reinforcement permits the economics of fiber combination system to be calculated for wide ranges of fiber loading and resin and fiber cost.

Effect of Fiber Loading

The Young's modulus of composite reinforced with Franklin Fiber® H-45 as a function of fiber loading is shown in Figure 4. Jeffamine EDR-148 (37 g /100 g ESO) and fumed silica (13 g/100 g ESO) were used in the formulation. It can be seen that the increase in fiber content leads to an increase in the tensile modulus at least up to 23 wt %, which subsequently levels off at loadings beyond this point. A explanation for this phenomenon is that higher fiber loading makes it difficult to evenly mix with the polymer matrix. The poor dispersion of the fibers and reduced interfacial adhesion to the polymer matrix may explain this reduction, because the effective transfer of stress between matrix and filler requires an adequate interfacial bonding. In the case of fiber-reinforced composites, it is well known that there exists a critical aspect ratio at which the mechanical properties of the composites are maximized. This critical aspect ratio depends on the volume fraction of the fiber and also on the ratio of the modulus of fiber to the matrix modulus.[12] In our system, increasing the volume fraction of the fiber further results in a slurry, which will not flow through the needle. Therefore data for higher Franklin fiber contents are not available.

Dynamic Mechanical Analysis

Dynamic mechanical analysis measurements were conducted on composite materials filled 12 vol % glass fiber, carbon fiber, Franklin fiber®

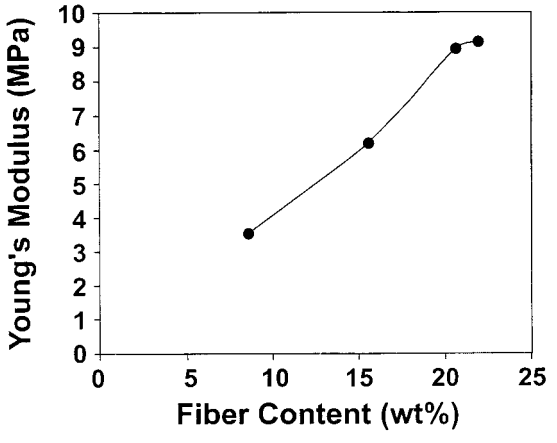

Figure 4 Modulus of Franklin fiber® H-45-filled composites versus fiber loading.

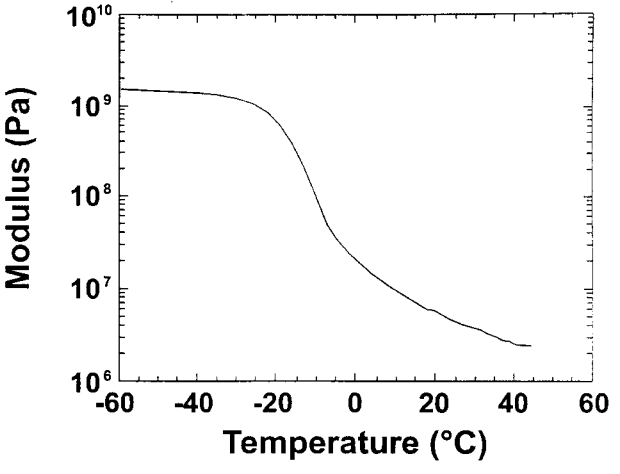

Figure 5 Modulus of Franklin fiber® H-45-filled composite versus temperature.

Table VI Dynamic Mechanical Data of Composites Filled with Four Different Fibers[a]

Fiber	Modulus (MPa)	T_g (°C)
Glass	1500	−20
Carbon	120	−17
Fillex® 17-AF1	55	−18
Franklin Fiber® H-45	24	−16

[a] Conditions: fiber, 12 vol %; Jeffamine EDR-148, 37 g/100 g ESO; fumed silica, 13 g/100 g ESO.

H-45, and Fillex® 17-AF1 fiber. A typical curve of modulus versus temperature is displayed in Figure 5 for E-glass filled composite. The summary of moduli at −60 °C and glass transition temperatures (T_g) for composites filled with four different fibers are presented in Table VI. The modulus of bend specimen with glass fiber is larger than carbon fiber, Wollastonite fiber, and Franklin fiber. However, theT_gs for composites prepared by using four different kinds of fibers as filler are almost identical around −18 °C.

CONCLUSIONS

The following conclusion may be drawn from the studies just presented. The extrusion freeform fabrication method can be used to form shapes from epoxidized soybean oil reinforced with glass, short carbon, Franklin Fiber® H-45, and Fillex® 17-AF1 fibers. In principle, these layerwise methods of building parts to be formed by chemical solidification do not require very long reaction times. Dynamic mechanical analysis measurements have shown that modulus of composite filled with glass fiber is larger than that filled with carbon, Wollastonite, and Franklin fibers. Four different kinds of fibers were used to prepare the composites, and all of them showed that T_gs are almost identical around −18 °C. In any stretching flow, the fiber rotates quickly towards the direction of greatest stretching. Freeform fabrication can result in highly aligned short-fiber composites. It can be seen that modulus is parallel to the writing direction much more often than normal to this direction. This result is significant because the composite modulus is at least as sensitive to orientation as to fiber aspect ratio and volume fraction.

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